Types of Occurrence of Nontronite and Nontronite-like Minerals in Soils[1]

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Nontronite, the iron-rich dioctahedral mineral of the montmorillonite group, is rarely found in soils. A number of montmorillonite clays having a high content of iron oxide have been found in subsoils. These occurrences are located at Toowoomba, Queensland, Australia; Waipata, South Island, New Zealand; Molumolu, Fiji; and at a number of sites in the Hawaiian Islands. These clays occur as relatively pure mineral aggregates and therefore are well segregated from their matrix. The type of occurrence provided material of homogeneous chemical and mineral compositions. The iron oxide content of these clays ranged from 9 to 32 per cent and indicates a wide range of iron substitution in the octahedral position. These clays occur under a wide range of climatic conditions, as evidenced by rainfall variation of 13 to 120 inches per year. Likewise, they occur in both early and late stages of weathering and, because of that, they occur in different mineral associations of primary minerals, other 2:1 clays, kaolin, iron oxides, and bauxite.

The purpose of this report is to describe the mode of the occurrence of these clays, the climatic environment, the weathering stage and mineral association, and their chemical and mineral composition.

The occurrence of nontronite in weathering basalt has been described by Allen and Schied (1946) in Washington. These nontronites are dioctahedral montmorillonite clays in which there is a full substitution of iron in the octahedral position. There is a similarity in the occurrence of some of the clays described in this report to the nontronite of Manato, Washington.

DESCRIPTION OF NONTRONITE OCCURRENCES

The description of the occurrences of nontronite and nontronite-like minerals will relate both their mode of occurrence and the climatic and weathering environments under which they exist. The climatic environment is divided into three types. The mineral weathering conditions are determined by the climatic conditions. The descriptions are as follows.

Semi-Arid Conditions

1. Lualualei, Oahu, Hawaii. A yellowish-green nontronite was found as one of the first products of weathering of olivine and as fragmental crystalline coatings on olivine in a picrite basalt, oceanite. It occurred in several boulders of a weathering picrite basalt exposed in the road cut across from the new Permanente Cement Plant on the Kolekole Pass Road. In many of the weathered olivine pockets in the rock, the unweathered green olivine crystals occurred in the center surrounded by yellowish-green, waxy-surfaced aggregates of nontronite. There is evidence that the nontronite may occur as pore fillings after weathering of the nontronite. Similar pore fillings with montmorillonite have been described by Sherman and Uehara (1956). The area receives about 15 inches of rainfall per year.

2. Road cut at Molumolu near Nandi, Fiji. Nontronite occurs as light yellowish-brown coating on peds and slickenslide surfaces. It also is impregnated in the pores of the peds. The soil of the peds is a black, sticky montmorillonite clay. The very nature of the occurrence suggested that the nontronitic clay was a secondary deposition of material from percolating leaching

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waters. This material was identified as nontronite by the New Zealand Division of Scientific and Industrial Research Laboratories. The rainfall in this area is between 15 and 20 inches per year.

Moderate Rainfall Areas

1. Waipata, South Island, New Zealand. This nontronite occurred as dark greenish-brown, elongated, waxy-coated mineral aggregates under a ledge of weathering basalt. This site was a protected accumulation area under a basalt boulder where the material would lose water slowly while continually receiving additional dissolved and suspended materials in the percolating waters. The mineral aggregates were extremely homogeneous in physical appearance. The climate was cool temperate, and the area received approximately 35 inches of rainfall per year.

2. Toowoomba, Queensland, Australia. This nontronite occurs as waxy, greenish-brown mineral aggregates in a lens near the top of a well-weathered basalt. The mineral aggregates occur both as elongated aggregated coatings on weathered basalt fragments and as independent units. The mineral aggregates are homogeneous and appear to be secondary deposition. The area is located due west of Brisbane and probably receives 35 inches of rainfall per year. Climate is subtropical.

Humid Tropical Rainforest Areas

1. Kahakuloa, West Maui, Hawaii. A greenish-yellowish-brown, waxy nontronite occurs as continuous layer coating in water drainage channels in a weathering oligoclase andesite of the Honolua flows of West Maui. This layer may be in close contact with halloysite clays. The climate is tropical and the rainfall is about 80 inches per year.

2. Nuuanu Pali, Oahu, Hawaii. Two samples of nontronite were collected from the contact zone of a vertical dike complex in the road cut on the windward side of the famous Pali on Oahu. The nontronite occurs as a layer at the contact zone of the dike. It is a waxy, greenish-gray-brown to greenish-brown mineral aggregate breaking into slightly curved aggregates with sharp points. The internal fracture faces are not always waxy in appearance. The climate is tropical with a rainfall of about 65 inches per year.

3. Wailua Reservoir, Kauai, Hawaii. In studying a weathered basalt boulder which had an unweathered rock core, green, waxy crystal aggregates were found. On further investigation, the crystals were quite numerous at the weathering contact zone and also in various locations in the highly weathered matrix of the shell of the weathered boulder. The nontronite was found in the following locations in this weathering rock system: (a) green, waxy nontronite crystals were found in the protective pockets in the rock and at the weathering contact zone; (b) waxy, green nontronite nodules occurred as pore fillings in the weathered portion of the rock; and (c) yellowish-green, waxy mineral aggregates occurred as segregated material in the weathered portion of the rock. The weathered portion of the rock is a ferruginous bauxite. The sample used in this study is contaminated with some gibbsite. The occurrence of these two minerals together is unique in nature. This area is a true humid tropical area with an annual rainfall of 100 inches or more.

CHEMICAL COMPOSITION OF NONTRONITES

The chemical composition of the nontronites was determined by standard sodium carbonate fusion. The results of the chemical analysis are given in Table 1. In considering the chemical analysis of these nontronites, some of the samples were difficult to collect without impurities. The samples collected at Lualualei may contain some olivine; the samples collected at Kahakuloa, Maui, may contain some halloysite and gibbsite; the Molumolu sample may contain some of the montmorillonite clay; and lastly the Wailua sample does have gibbsite impregnated in it. The gibbsite interfingering was clearly discerned by petrographic examination of thin sections. However, in each case every effort was made to obtain as pure a sample as possible.

The samples from Lualualei and Toowoomba have a high content of magnesium. Some of the magnesium in the Lualualei sample may come from the olivine which contains 46 per cent MgO. The samples collected at Molumolu and Waipata have moderate amounts of MgO,

TABLE 1

THE CHEMICAL COMPOSITION OF NONTRONITES SAMPLED UNDER A WIDE RANGE OF CLIMATIC AND WEATHERING ENVIRONMENTS

CONSTITUENT	SEMIARID		MODERATE RAINFALL		HUMID TROPICAL				STANDARD NONTRONITE
	Lualualei Valley, Oahu, Hawaii	Molumolu, Fiji	Waipata, S. Island, New Zealand	Toowoomba, Queensland, Australia	Kahakuloa, Maui, Hawaii	Nuuanu Pali, Oahu, Hawaii		Wailua Game Refuge, Kauai, Hawaii	
	weathering product after olivine	clay coating, skins, impregnations	under weathering basalt boulder	pockets in subsoil of lateritic soil formed from basalt	mineralized drainage channel	volcanic dike weathered basalt	contact zone to dike in weathered basalt	weathered basalt boulder	
	%	%							
SiO_2	48.20	52.28	48.54	48.74	33.35	39.04	43.69	26.40	45.83
Al_2O_3	7.02	21.43	16.88	21.02	22.65	23.73	17.65	28.00	5.05
Fe_2O_3	16.39	9.95	15.52	8.82	31.52	17.13	14.18	26.26	36.44
TiO_2	0.58	0.92	0.77	0.53	0.35	3.01	2.61	2.01	0.49
CaO	4.26	1.18	2.30	1.29	0.01	0.55	3.52	0.10	2.20
MgO	17.12	4.39	6.72	10.71	0.21	0.69	0.75	0.73	1.14
K_2O	0.00	1.52	0.21	0.08	0.12	0.00	0.16	0.00	0.00
Na_2O	0.53	2.43	0.37	0.48	1.29	0.49	3.01	0.00	0.00
MnO	0.16	0.06	0.03	0.06	0.08	0.34	0.20	0.08	0.02
P_2O_5	0.00	0.07	0.04	0.21	0.05	0.04	0.03	0.11	—
Loss on Ignition	6.87	8.67	9.94	10.86	10.70	12.78	9.65	15.77	9.12

4.4 and 6.7 per cent respectively. All of the other samples are low in magnesium.

The Fe_2O_3 content of the nontronites and nontronite-like samples ranged from 8.8 to 31.5 per cent. The samples collected at Toowoomba and Molumolu had the lowest Fe_2O_3 content, 8.8 and 9.9 per cent respectively. The Fe_2O_3 content of the samples collected at Lualualei, Waipata, and Nuuanu Pali ranges from 14.2 to 17.1 per cent. The samples collected at Kahakuloa, Wailua, and the *standard nontronite* sample from Manato, Washington, have a much higher Fe_2O_3 content. The Wailua nontronite contains gibbsite; and, if the sample were corrected for its gibbsite content, the Fe_2O_3 would probably equal that of the other samples. The correction is made by using the increase in per cent lost on ignition as indication of gibbsite content.

The alumina content is high (16.9 to 28.0 per cent) in all samples except the Lualualei sample and the standard nontronite sample.

The silica content ranges from 43.7 to 52.3 per cent in all samples except the samples collected at Kahakuloa and Wailua, which contained 33.4 and 26.4 per cent respectively.

Only the samples collected at Waipata, New Zealand, have a calcium content comparable to the standard nontronite sample from Manato, Washington. The samples collected at Lualualei and one at the Nuuanu Pali had a much higher content of calcium, and all others were considerably lower.

The high titanium content in the three Hawaiian samples is a residual enrichment from the parent basalt, which has a high titanium content, as pointed out by Cross (1915).

MINERAL IDENTIFICATION OF NONTRONITE

Examination of the X-ray data shows two pertinent features of the Wailua clay: first, that the clay is a montmorillonite type clay; and, second, a more conjectural one, that the ion substitution in the octahedral layer might be ferruginous in nature. X-ray analysis of the oriented, glycerol-solvated clay showing a strong 001 basal reflection at 17.7Å, verifies the first, but the second statement requires some explanation.

The diffraction pattern in Figure 1 is that of powder samples, but the strong 001 line indicates some degree of preferred orientation in that plane. An increase in the b-axial length of the montmorillonite group of minerals in the order montmorillonite—nontronite—saponite clays had been suggested by Brindley (1951). Measurement of the 060 index for Wyoming bentonite, Washington nontronite, and the Wailua clay shows a sequence: Wyoming bentonite—nontronite—Wailua nontronite. The axial length of the Wailua clay is intermediate to that of Wyoming bentonite and Washington nontronite. The b-axial length of nontronite and saponite are, however, so alike that it is impossible to differentiate between these two minerals by X-ray technique alone. Chemical data must be used to support any claim to the identification of the mineral.

DISCUSSION OF RESULTS

The data presented in this report show a wide range in the chemical composition of the nontronite or nontronite-like minerals. If one were to use the degree of substitution of iron in the octahedral position as the criterion, then not all of these 2:1 minerals could be considered nontronite. If a 50 per cent or more substitution of iron were used as a criterion for nontronite, the minerals from Toowoomba and Lualualei would not qualify. The sample at Toowoomba cannot be considered to be a nontronite; but probably, at best, it would be a magnesium nontronite or more likely an iron saponite. This was borne out by the X-ray diffraction pattern for this sample in that it favored a trioctahedral structure more than the Wailua sample's pattern. The other low iron oxide-containing mineral was the sample from Molumolu, Fiji. However, here the magnesium content is low. Thus, a dioctahedral structure is possible with a low iron substitution.

All other samples contained sufficient iron oxide content to support a 50 per cent or more substitution of iron in the octahedral position.

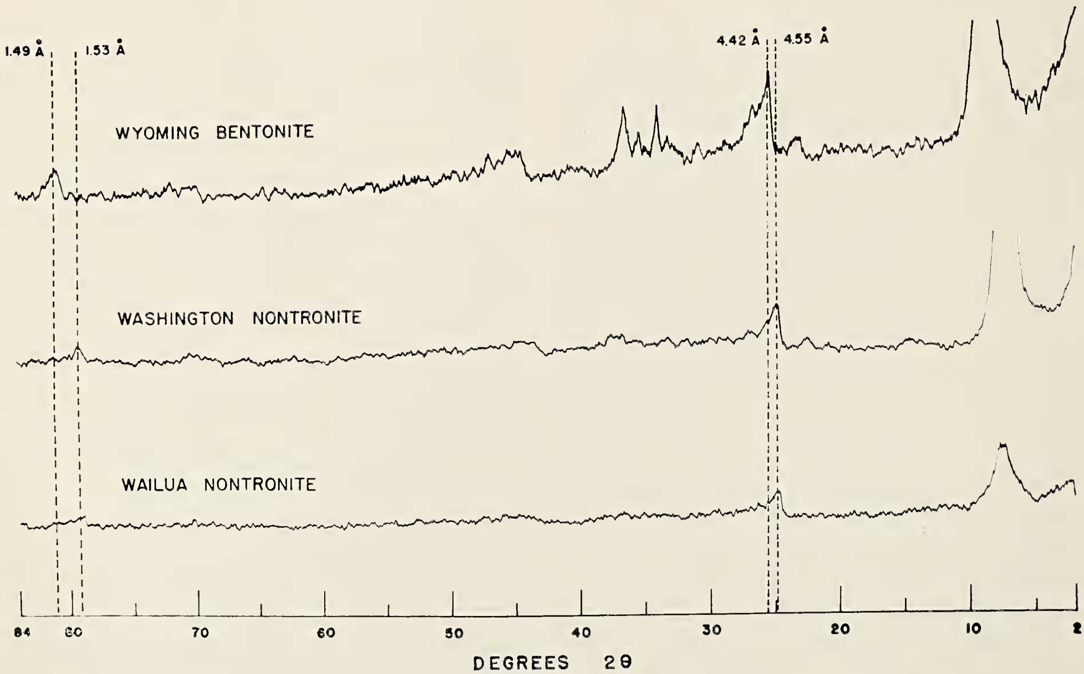

FIG. 1. X-ray diffractometer traces of Wyoming bentonite, Washington nontronite, and Wailua nontronite.

The X-ray diffraction patterns favor the nontronite identification. The sample from Wailua, Kauai, had a pattern almost identical with that of the standard nontronite from Manato, Washington.

The occurrence of nontronite in these locations suggests several interpretations of the weathering processes which are involved. The mode of occurrence suggests that both the climatic environment and the type of weathering system have a strong effect on the nature of the clay mineral formed. In each instance, these clay minerals have formed as secondary minerals with more or less complete separation from other minerals. Even in the Lualualei sample, the nontronitic clay has clearly separated from olivine.

The Fe_2O_3 content of these clays has ranged from 8.8 to 31.5 per cent. The Fe_2O_3 content probably reflects the concentration of active Fe in the weathering system rather than any other factor. The high Fe_2O_3 content in the Lualualei sample and its high magnesium content reflect the release of ions from the decomposing olivine and the possible migration of Fe from the weathering matrix to the cavity produced by loss of volume of the olivine. The source of iron must come from the matrix, as the olivine is iron poor. Sherman and Uehara (1956) have described a 2:1 montmorillonitic clay having a high content of Fe_2O_3 occurring after olivine in the same type of rock. Since their clay had a much lower MgO content, we suggest that in time Fe will replace Mg and produce a nontronitic clay.

The content of bases is higher in the dryer areas. This is what one would expect. The low base content of the nontronite samples from the humid area suggests that these clays have formed under conditions of strong leaching and good drainage. The high content of Fe_2O_3 in these clays further suggests that the concentration of Fe has been sufficiently high and continuous to produce a high degree of Fe inclusion in the crystal lattice. However, the stability of this mineral in this type of a system would not be expected in this environment favorable for weathering and leaching. Stability would have to arise from the presence of a continuous source of silica and Fe to maintain the stability of the nontronite mineral, or otherwise some other protective system must exist, such as an impervious coating of either halloysite, iron oxide, or gibbsite. The stability of the nontronites found at Kahakuloa and Nuuanu Pali can be explained by the former condition, in that they occur in a position in which leachates from adjacent weathering rocks move through or near these clays. These leachates may contain sufficient Fe and Si to maintain the stability of the nontronite. In the Kahakuloa area there is evidence that the nontronite will decompose with the loss of SiO_2, and iron oxide mineral will form. A similar system has been proposed by Bates (1960) for the halloysite-gibbsite system in the same weathering rock formation. There is an indication in these occurrences that nontronite might be more stable than heretofore observed by workers.

The weathering rock from the Wailua sample has been the object of many investigations. Abbott (1958) and Sherman *et al.* (1962) have described the bauxitic weathering of this rock. The weathering of this rock is characterized by its rapid loss of bases and desilication. Almost at the contact zone with the rock core, the bases have been reduced to trace quantities, and the SiO_2 has been reduced from 40 per cent in the rock to 2 per cent in the weathering product. The nontronite mineral aggregates, and nodular pore fillings, have almost identical X-ray patterns with that of the standard nontronite sample. The nontronites occurring near the weathering contact zone owe their stability to the protective effects of the rock. The stability of the nontronite pore filling and aggregates in the weathering matrix is more of a puzzle. The close association with gibbsite has been observed in the X-ray diffraction patterns as well as in thin sections. At this point, the stability of nontronite in this association cannot be explained except that it must be more resistant to decomposition than was previously suspected. However, there is a suggestion that the nontronite will decompose to iron oxide minerals in time. Iron oxide minerals occurring as pore filling or replacements are numerous in similar locations in the weathering matrix, thus suggesting the eventual decomposition of nontronite by desilication.

SUMMARY

This study describes the mode of occurrence of eight nontronite and nontronite-like minerals occurring in Australia, New Zealand, Fiji, and Hawaii. Each of the minerals has a relatively high content of Fe_2O_3, ranging from 8.8 to 31.5 per cent. Six of these minerals contain sufficient Fe_2O_3 to be considered a nontronite.

The chemical composition suggests that the degree of iron substitution in the octahedral position is related to the concentration of the Fe. The iron oxide content of these 2:1 layered silicate minerals appears to increase as weathering of silicate minerals approach completion.

X-ray diffraction supports the identification of nontronite. The sample from a ferruginous bauxite boulder gave X-ray patterns almost identical to that of a standard nontronite sample from Manato, Washington.

The occurrence of nontronite in a bauxite suggests that the stability of the mineral must be due either to the concentration of Fe and Si in the percolating waters, or to possible protective mineral coatings, or to greater resistance to weathering and leaching than has been previously considered.

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